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# (54) Refrigerating machine oil composition

Ölzusammensetzung für Kältemaschinen Composition d'huile pour machine réfrigérante

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### Description

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# BACKGROUND OF THE INVENTION

### 1. Field of the Invention

[0001] The present invention relates to a refrigerating machine oil composition. More particularly, it pertains to a refrigerating machine oil composition which is excellent in stability, sludge preventive properties and copper-plating preventive properties.

### 2. Description of Related Art

[0002] There have heretofore been employed a variety of refrigerating machine oils as the lubricating oils for various refrigerating machines to be used in automobile air conditioners, refrigerators, room air conditioners and the like. Since such refrigerating machine oils are in use for a long period of time, they are required to be highly reliable.

[0003] However, such various disadvantages are pointed out in the conventional refrigerating machine oils as the generation of copper plating, unsatisfactory stability, rise in total acid number and sludge formation. In view of the above, there are proposed and used the compositions comprising various base oils in various combination with additives.

[0004] Nevertheless, it can not be said that any of the above-proposed compositions now in use is satisfactory from the viewpoint of practical application. In particular, importance has been attached to environmental problems in recent years with the result that the use of a specified flon refrigerant was sustained which threatens destruction of the ozone layer. Herein, flon means fluorochlorocarbon, fluorochlorohydrocarbon, fluorohydrocarbon or fluorocarbon. Consequently, some alternative refrigerants have emerged, and thus it is hoped that a refrigerating machine oil well suited to such refrigerants will be developed as early as possible.

[0005] The research and development of such refrigerating machine oil, however, are only in the very beginning, revealing the actual situation that the achievement therefrom is not yet sufficient.

[0006] US-4,431,557 discloses a fluid composition comprised of a fluorocarbon refrigerant, a hydrocarbon oil and an alkylene oxide additive compound. The additive is said to improve the thermal resistance of the oil in the presence of the refrigerant.

[0007] DE-A-2820640 discloses a highly viscous oil composition for refrigerating machines comprising a polyglycol oil having a kinematic viscosity of 50 - 200 cSt at 98,9° C and a viscosity index of at least 150 and 0,1 - 10 % by weight of at least one compound from the group comprising epoxy compounds of either the glycidylether, epoxydized fatty acid monoester and epoxydized vegetable oil type.

[0008] US-2,552,084 discloses a fluid for use in refrigerating systems comprising a halogenated hydrocarbon refrigerant and lubricant either with or without an antifreeze and one or more organic oxides of the epoxy type acting as an inhibitor or stabilizer.

[0009] However, none of the above-mentioned documents mentions or discloses the specific expoxides defined in the present invention.

[0010] Under such circumstances, intensive research and development were made by the present inventor in order to develop a refrigerating machine oil which is excellent in stability, sludge preventive properties and copper-plating preventive properties, capable of being used with high reliability over a long period of time, and also well suited not only to the conventional specified flon refrigerants but also to various alternative refrigerants free from the fear of causing environmental pollution.

[0011] As a result, it has been found by the present inventor that the objective performance is satisfied by the composition comprising a base oil blended with a specific epoxy compound. Thus, the present invention has been accomplished on the basis of the above-mentioned finding and information.

### SUMMARY OF THE INVENTION

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[0012] The present invention provides a refrigerating machine oil composition which comprises a base oil blended with a specific epoxy compound. In particular, the present invention provides a refrigerating machine oil composition which comprises a base oil blended with at least one epoxy compound selected from the group consisting of D-limonene oxide, L-limonene oxide, α-pinene oxide and L-carvone oxide.

[0013] The refrigerating machine oil composition according to the present invention is employed in a variety of refrigerating machines, and is well suited for use in a compression type refrigerating cycle which is usually composed at least of a compressor, a condenser, an expansion valve or a capillary tube and an evaporator.

### DESCRIPTION OF PREFERRED EMBODIMENT

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[0014] The base oil to be used in the refrigerating machine oil composition as the lubricating oil according to the present invention is exemplified by various base oils such as those which have heretofore been used in the refrigerating machine oil without specific limitation. The kinematic viscosity of the base oil to be used is usually 5 to 500 cSt at 40°C, preferably 10 to 300 cSt at 40°C.

The type of the base oil may be either a mineral oil or a synthetic oil, and is preferably at least one oxygenatom-containing compound selected from the group consisting of a polyglycol and a polyvinyl ether or a mixture of said compound and a hydrocarbon compound.

[0016] A wide variety of polyglycols are available. Preferable examples among them include a polyglycol represented by the general formula II (polyoxyalkylene glycol derivative)

$$R^{3}[(OR^{4})_{m}OR^{5}]_{n} \tag{II}$$

wherein R<sup>3</sup> is a hydrogen atom or an alkyl group having 1 to 10 carbon atoms, R<sup>4</sup> is an alkylene group having 1 to 10 carbon atoms, R<sup>5</sup> is a hydrogen atom or an alkyl group having 1 to 10 carbon atoms, n is an integer of 1 to 6, preferably 1, and m is such a number that causes the average of m x n to be 6 to 80. (Refer to Japanese Patent Application Laid-Open No. 305893/1990.)

[0017] Specific examples of the polyglycols include polyoxypropylene glycol, mono or di-methyl ether derivative of polyoxypropylene glycol [for example,  $CH_3O(CH(CH_3)\ CH_2O)_mCH_3$ ], mono or di-ethyl ether derivative of polyoxypropylene glycol, mono-n-butyl ether derivative of polyoxypropylene glycol, polyoxyethylene glycol, mono or dimethyl ether derivative of polyoxyethylene glycol [for example,  $CH_3O(CH(CH_3)CH_2O)_x(CH_2CH_2O)_y-CH_3$ ; x+y=m].

[0018] On the other hand, a wide variety of polyvinyl ethers are available. Preferable examples among them include a vinyl ether-based polymer having the constitutional unit represented by the general formula (III)

wherein R<sup>6</sup>, R<sup>7</sup> and R<sup>8</sup> are each a hydrogen atom or a hydrocarbon radical, especially an alkyl group, having 1 to 10 carbon atoms; R<sup>9</sup> is a divalent hydrocarbon radical, especially an alkylene group, having 1 to 10 carbon atoms or a divalent ether-linkage oxygen atom-containing hydrocarbon radical, especially an alkoxy group-containing alkylene group, having 2 to 20 carbon atoms; R<sup>10</sup> is a hydrocarbon radical, especially an alkylene group, having 1 to 10 carbon atoms; k is a number from 0 to 10, preferably 0 to 5 in average; R<sup>6</sup> to R<sup>10</sup> may be the same as or different from each other per each constitutional unit; and R<sup>9</sup>, when contained in plural in the constitutional units, may be the same or different.

[0019] Specific examples of the polyvinyl ethers include poly(vinyl ethyl ether) [for example, CH<sub>3</sub>CH<sub>2</sub>O[CH<sub>2</sub>CH (OCH<sub>2</sub>CH<sub>3</sub>)]<sub>i</sub>H wherein i is an integer], poly(vinyl octyl ether) and poly(vinyl butoxypropyl ether).

[0020] The hydrocarbon compound to be employed in the form of mixture with the above-mentioned polyglycol or polyvinyl ether is exemplified by a mineral oil, an olefinic polymer and a synthetic oil such as alkylbenzene and alkylnaphthalene each having a kinematic viscosity at 40°C of 5 to 500 cSt, preferably 10 to 300 cSt. Preferable oils among them are alkylbenzene in which the total number of carbon atoms in alkyl group(s) is 1 to 50 and alkylnaphthalene in which the total number of carbon atoms in alkyl group(s) is 1 to 50.

[0021] As mentioned hereinbefore, the preferable examples of the base oil to be used in the refrigerating machine oil composition as the lubricating oil according to the present invention include at least one oxygen-atom-containing compound selected from the polyglycol and the polyvinyl ether or a mixture of said compound and the aforesaid hydrocarbon compound. In the case where a mixture of the oxygen-atom-containing compound and the hydrocarbon compound is employed, the ratio of the former compound to the latter compound may be suitably selected according to the situation, and is determined in the range of preferably 100/0 to 10/90 by weight.

[0022] Aside from the foregoing, the epoxy compound to be blended with the above-mentioned base oil is at least one epoxy compound selected from the group consisting of D-limonene oxide, L-limonene oxide,  $\alpha$ -pinene oxide and

L-carvone oxide.

[0023] The aforestated epoxy compound is employed alone or in combination with at least one other epoxy compound as exemplified above.

[0024] The compounding ratio of the above-mentioned epoxy compound in the refrigerating machine oil according to the present invention varies depending on various conditions and can not unequivocally be determined. However, it is selected in the range of usually 0.05 to 10% by weight, preferably 0.2 to 5% by weight based on the whole composition. An unreasonably low compounding ratio of the epoxy compound leads to difficulty in achieving the expected effect, whereas an excessively high compounding ratio thereof results in failure to attain the effect which is directly proportional to the compounding ratio.

[0025] As described hereinbefore, the refrigerating machine oil composition according to the present invention comprises the aforestated base oil and epoxy compound, but may further comprise, when desired, any of various additives that are in use in the conventional lubricating oils such as extreme pressure agent, stabilizing agent, metal deactivator (especially copper deactivator), defoaming agent, chlorine scavenger, detergent-dispersant, viscosity-index improver, oiliness agent, abrasion-resistant additive, rust preventive, corrosion inhibitor and pour point depressant.

[0026] As the extreme pressure agent, there can be mentioned a phosphoric ester and a phosphorous ester. As the stabilizing agent, there can be mentioned a phenol-based antioxidant, an amine-based antioxidant and an epoxy-based antioxidant (phenylglycidyl ether, cyclohexene oxide, epoxidized soybean oil, etc.). As the copper deactivator, mention can be made of benzotriazole and a derivative thereof. As the defoaming agent, mention can be made of silicone oil (dimethylpolysiloxane, etc.) and fluorinated silicone.

[0027] The refrigerating machine oil composition according to the present invention is excellent in compatibility not only with the conventional specified flon refrigerants but also with various alternative flon refrigerants that have been developed in recent years. Consequently, the refrigerating machine oil composition according to the present invention is well suited for the lubrication of refrigerating machines, especially compression type refrigerating machines in which different kinds of flon refrigerants are employed.

[0028] Examples of the flon refrigerants that are used in the refrigerating machines include R134a(1,1,1,2-tetrafluoroethane, R12(dichlorodifluoromethane), R22(chlorodifluoromethane), R502[azeotropic mixture of R22 and R115 (1-chloro-1,1,2,2,2-pentafluoroethane), R152a(1,1-difluoroethane), R125(1,1,1,2,2-pentafluoroethane), R143a (1,1,1-trifluoroethane), R32(difluoromethane), R23(trifluoromethane), R225cb(1,3-dichloro-1,1,2,2,3-pentafluoropropane), R225ca(1,1-dichloro-2,2,3,3,3-pentafluoropropane), R141b(1,1-dichloro-1-fluoroethane), R123(1,1-dichloro-2,2,2-trifluoroethane), R142b(1-chloro-1,1-difluoroethane) and R124(1-chloro-1,2,2,2-tetrafluoroethane). Particularly preferable flon refrigerants among them are those not containing chlorine atom, that is, a fluorohydrocarbon series flon refrigerant from the viewpoint of preventing environmental destruction.

[0029] As described hereinbefore, the refrigerating machine oil composition according to the present invention is excellent in stability, sludge preventive properties and copper-plating preventive properties and at the same time, exhibits excellent compatibility not only with the conventional specified flon refrigerants but also with various alternative flon refrigerants free from the fear of causing environmental pollution.

[0030] Therefore, the refrigerating machine oil composition according to the present invention is particularly effective for use in automobile air conditioner, room air conditioners, refrigerators and the like, thus rendering itself extremely valuable from the standpoint of industrial utilization.

[0031] In the following, the present invention will be described in more detail with reference to the examples and the comparative examples, which however shall not be construed to limit the present invention thereto.

## Comparative Examples 1 to 3

[0032] Refrigerating machine oil compositions as lubricating oils were prepared by the use of the base oils each having the physical properties as given in Table 1 and by blending any of various epoxy compounds therewith.

[0033] The symbols of the base oils in Tables 1 to 5 are described in detail as follows:

PAG: polyalkylene glycol (polypropylene glycol dimethyl ether)

50 PVE: polyvinyl ether [poly(vinyl ethyl ether)]

Alkylbenzene: dodecylbenzene

polycarbonate (polypropylene glycol polycarbonate)

Ester: dipentaerythritol hexahexanoate

PC:

Table 1

(Physica	al propert	ies of bas	se oils)		
Physical properties			Type		
	PAG	PVE	Alkylbenzene	PC	Ester
Kinematic viscosity at 40°C (cSt) Kinematic viscosity at 100°C (cSt) Viscosity index	42.69 9.384 212	41.99 5.961 79	37.81 4.679 -32	111.8 10.28 62	71.97 10.04 122

[0034] Thereafter, in a 250 ml pressure resistant vessel were placed 50 g of any of the above-prepared refrigerating machine oil compositions, 25 g of R134a as the refrigerant, 100 ml of air, water in a proportion of 0.5% by weight based on the oil composition and a catalyst comprising iron, copper and aluminum, and the vessel was hermetically sealed and then allowed to stand at 175°C for 10 days. Thereafter the vessel was opened, and investigations were made on the appearance of the oil composition, the appearance of the catalyst, the total acid number of the oil composition and the formation of any sludge. The results are given in Table 2.

[0035] The symbols of the epoxy compounds (A to C) in Tables 1 to 5 are described in detail as follows:

- A: D-limonene oxide
- B: α-pinene oxide

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C: L-carvone oxide

Table 2 (Refrigerant : R134a)

No.	Base oil type am	oil amount(wt8)	Bpox	Bpoxy compound type amount(wt%)	Appearance of Appearance Total acid Sludge oil composition of catalyst number formatic	Appearance of catalyst	Total acid	Sludge formation
Comparative Example 1	PAG	100	1	ŧ	yellow	pood	9.0	not formed
Comparative Example 2	PVB	100	1	1	yellow	pood	0.7	not formed
Comparative Example 3	Comparative alkylbenzene Bxample 3	100	ī	1	yellow	dood	. e. 0	not formed

## Comparative Examples 4 to 7

[0036] Refrigerating machine oil compositions as lubricating oils were prepared by the use of the base oils each having the physical properties as given in Table 1 and by blending any of various epoxy compounds therewith.

[0037] Thereafter, in a 250 ml pressure resistant vessel were placed 50 g of any of the above-prepared refrigerating machine oil compositions, 25 g of R12 as the refrigerant, 100 ml of air, water in a proportion of 0.5% by weight based on the oil composition and a catalyst comprising iron, copper and aluminum, and the vessel was hermetically sealed and then allowed to stand at 175°C for 10 days. Thereafter the vessel was opened, and investigations were made on the appearance of the oil composition, the appearance of the catalyst, the total acid number of the oil composition and the formation of any sludge. The results are given in Table 3.

Table 3 (Refrigerant : R12)

Total acid Sludge number formation	13 formed	14 formed	29 formed	13 formed
Total				
Appearance of catalyst	copper-plating formed	copper-plating formed	copper-plating formed	copper-plating formed
Appearance of oil composition	black	black	black	black
Epoxy compound	ı	ı	ţ	1
Ероху <u>type</u> a	ı	1	t	i
Base oil amount(wt%)	100	100	100	100
Ваве	PAG	PVB	Bster	24
NO.	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7

# Examples 14 to 21 and Comparative Examples 8 to 10

[0038] Refrigerating machine oil compositions as lubricating oils were prepared by the use of the base oils each having physical properties as given in Table 1 and by blending any of various epoxy compound therewith.

[0039] Thereafter, in a 250 ml pressure resistant vessel were placed 50 g of any of the above-prepared refrigerating machine oil compositions, 25 g of R134a as the refrigerant, 100 ml of air, water in a proportion of 0.5% by weight based on the oil composition and a catalyst comprising iron, copper and aluminum, and the vessel was hermetically sealed and then allowed to stand at 175°C for 10 days. Thereafter the vessel was opened, and investigations were made on the appearance of the oil composition, the appearance of the catalyst, the total acid number of the oil composition and the formation of any sludge. The results are given in Table 4.

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Table 4 (Refrigerant : R134a)

Ño.	Bas	Base oil	Bpox	Rpoxy compound	Appearance of	Appearance	Total acid	Sludge
	type	amount (wt8)	type	amount (wt8)	oil composition	of catalyst	number	formation
Example	1 PAG	98.0	۵	2.0	poob	good	0.1>	not formed
Example	2 PAG	98.0	Ø	2.0	pood	good	0.1>	not formed
Example (	3 PAG	98.0	<u>p</u>	2.0	good	good	0.1>	not formed
Skample	4 PVB	98.0	Q	2.0	good	pood	0.1>	not formed
Example	5 9VB	98.0	M	2.0	good	good	0.1>	not formed
Example (	EVB 6	98.0	ĵs,	2.0	good	good	0.1>	not formed
Example	7 PAG alkylbenzene	50.0 ·	Ω	2.0	poob	good	0.1>	not formed
Example	8 PVE alkylbenzene	30.0 ane 68.0	<b>p.</b> ,	2.0	boop	good	0.1>	not formed
Comparative Example 8	ve PAG	100	1	•	yellow	poof	9.0	not formed
Comparative Example 9	ve PVE	100	ı	ı	yellow	good	0.7	not formed
Comparative Example 10	ve alkylbenzene 0	ane 100	ı	ı	yellow	good	0.3	not formed

# Examples 9 to 13 and Comparative Examples 11 to 14

[0040] Refrigerating machine oil compositions as lubricating oils were prepared by the use of the base oils each having the physical properties as given in Table 1 and by blending any of various epoxy compounds therewith.

[0041] Thereafter, in a 250 ml pressure resistant vessel were placed 50 g of any of the above-prepared refrigerating machine oil compositions, 25 g of R12 as the refrigerant, 100 ml of air, water in a proportion of 0.5% by weight based on the oil composition and a catalyst comprising iron, copper and aluminum, and the vessel was hermetically sealed and then allowed to stand at 175°C for 10 days. Thereafter the vessel was opened, and investigations were made on the appearance of the oil composition, the appearance of the catalyst, the total acid number of the oil composition and the formation of any sludge. The results are given in Table 5.

Table 5 (Refrigerant ; R12)

No.	Base oil type am	oil amount(wt%)	RPOX	Spory compound Ype amount(wt%)	Appearance of oil composition	Appearance of catalyst	Total acid number	Sludge formation
Example 9	PAG	98.0	۵	2.0	pood	good	0.1>	not formed
Example 10	PVA	98.0	M	2.0	poof	pood	0.1>	not formed
Bxample 11	PAG alkylbenzene	50.0	ΩÞ	1.0	poob	good	0.1>	not formed
Comparative Brample 11	PAG	100	ı	ı	black	copper-plating formed	£1	formed
Comparative Example 12	PVB	100	1	ı	black	copper-plating formed	14	formed
Example 12	Ester	98.0	Ω	2.0	brown	iron blackened	5.7	slightly formed
Example 13	2	98.0	μq	2.0	brown	iron blackened	6.0	slightly formed
Comparative Example 13	Bster	100	1	1	black	copper-plating formed	53	formed
Comparative Example 14	DG.	100	ı	1 .	black	copper-plating formed	£1	formed

#### Claims

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- A refrigerating machine oil composition which comprises a base oil and at least one epoxy compound selected from the group consisting of D-limonene oxide, L-limonene oxide, α-pinene oxide and L-carvone oxide, said epoxy compound being blended with said base oil.
- 2. The composition according to Claim 1 wherein the at least one epoxy compound selected from the group consisting of D-limonene oxide, L-limonene oxide, α-pinene oxide and L-carvone oxide is blended in an amount of 0.05 to 10% by weight based on the whole amount of the composition.
- 3. The composition according to Claim 1 wherein the base oil is at least one oxygen-atom-containing compound selected from the group consisting of polyglycol and polyvinyl ether.
- 4. The composition according to Claim 1 wherein the base oil is a mixture of a hydrocarbon compound and at least one oxygen-atom-containing compound selected from the group consisting of polyglycol and polyvinyl ether.
  - 5. The composition according to Claim 3 wherein the polyglycol is a polyoxyalkylene glycol derivative represented by the general formula (II)

$$R^{3}[(OR^{4})_{m}OR^{5}]_{n}$$
 (II)

Wherein  $\mathbb{R}^3$  is a hydrogen atom or an alkyl group having 1 to 10 carbon atoms,  $\mathbb{R}^4$  is an alkylene group having 1 to 10 carbon atoms,  $\mathbb{R}^5$  is a hydrogen atom or an alkyl group having 1 to 10 carbon atoms, n is an integer of 1 to 6, and m is such a number that causes the average of m x n to be 6 to 80.

6. The composition according to Claim 4 wherein the polyglycol is a polyalkylene glycol derivative represented by the general formula (II)

$$R^{3}[(OR^{4})_{m}OR^{5}]_{n}$$
 (II)

wherein  $\mathbb{R}^3$  is a hydrogen atom or an alkyl group having 1 to 10 carbon atoms,  $\mathbb{R}^4$  is an alkylene group having 1 to 10 carbon atoms,  $\mathbb{R}^5$  is a hydrogen atom or an alkyl group having 1 to 10 carbon atoms, n is an integer of 1 to 6, and m is such a number that causes the average of m x n to be 6 to 80.

7. The composition according to Claim 3 wherein the polyvinyl ether is a vinyl ether-based polymer having the constitutional unit represented by the general formula (III)

$$R^{6}$$
 $R^{8}$ 
 $C - C$ 
 $R^{7}$ 
 $O(R^{9}O)_{k}$ 
 $R^{10}$ 
(III)

wherein R6, R7 and R8 are each a hydrogen atom or a hydrocarbon radical, especially an alkyl group, having 1 to 10 carbon atoms; R9 is a divalent hydrocarbon radical, especially an alkylene group, having 1 to 10 carbon atoms or a divalent ether-linkage oxygen atom-containing hydrocarbon radical, having 2 to 20 carbon atoms; R10 is a hydrocarbon radical, especially an alkylene group, having 1 to 10 carbon atoms; k is a number from 0 to 10 in average; R6 to R10 may be the same as or different from each other per each constitutional unit; and R9, when contained in plural in the constitutional units, may be the same or different.

55 8. The composition according to Claim 4 wherein the polyvinyl ether is a vinyl ether-based polymer having the constitutional unit represented by the general formula (III)

wherein R<sup>6</sup>, R<sup>7</sup> and R<sup>8</sup> are each a hydrogen atom or a hydrocarbon radical, especially an alkyl group, having 1 to 10 carbon atoms; R<sup>9</sup> is a divalent hydrocarbon radical, especially an alkylene group, having 1 to 10 carbon atoms or a divalent ether-linkage oxygen atom-containing hydrocarbon radical, having 2 to 20 carbon atoms; R<sup>10</sup> is a hydrocarbon radical, especially an alkylene group, having 1 to 10 carbon atoms; k is a number from 0 to 10 in average; R<sup>6</sup> to R<sup>10</sup> may be the same as or different from each other per each constitutional unit; and R<sup>9</sup>, when contained in plural in the constitutional units, may be the same or different.

### Patentansprüche

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- Kältemaschinen-Ölzusammensetzung, die umfaßt: ein Grundöl und mindestens eine Epoxyverbindung, ausgewählt aus der Gruppe, die besteht aus D-Limonen-Oxid, L-Limonen-oxid, α-Pinen-Oxid und L-Carvon-Oxid, wobei die genannte Epoxyverbindung mit dem erwähnten Grundöl vermischt ist.
- Zusammensetzung nach Anspruch 1, worin mindestens eine Epoxygruppe, ausgewählt aus der Gruppe, die besteht aus D-Limonen-Oxid, L-Limonen-Oxid, α-Pinen-Oxid und L-Carvon-Oxid in einer Menge von 0,05 bis 10 Gew.-%, bezogen auf die Gesamtmenge der Zusammensetzung zugemischt ist.
  - 3. Zusammensetzung nach Anspruch 1, worin das Grundöl mindestens eine Sauerstoff-enthaltende Verbindung ist, die ausgewählt wird aus der Gruppe, die aus Polyglycolen und Polyvinylethern besteht.
- 20 4. Zusammensetzung nach Anspruch 1, worin das Grundöl eine Mischung einer Kohlenwasserstoffverbindung und mindestens einer Sauerstoff-enthaltenden Verbindung ist, die aus der Gruppe ausgewählt wird, die besteht aus Polyglycolen und Polyvinylethern.
- Zusammensetzung nach Anspruch 3, worin das Polyglycol ein Polyoxyalkylenglycolderivat, dargestellt durch die
   allgemeine Formel (II) ist

$$R^{3}[(OR^{4})_{m}OR^{5}]_{n}$$
 (II)

- worin R<sup>3</sup> ein Wasserstoffatom oder eine Alkylgruppe mit 1 bis 10 Kohlenstoffatomen ist, R<sup>4</sup> eine Alkylengruppe mit 1 bis 10 Kohlenstoffatomen ist, R<sup>5</sup> ein Wasserstoffatom oder eine Alkylgruppe mit 1 bis 10 Kohlenstoffatomen ist, n eine ganze Zahl von 1 bis 6 ist und m eine solche Zahl darstellt, daß der Durchschnittswert m x n bei 6 bis 80 liegt.
- Zusammensetzung nach Anspruch 4, worin das Polyglycol ein Polyalkylenglycolderivat ist, dargestellt durch die allgemeine Formel (II)

$$R^{3}[(OR^{4})_{m}OR^{5}]_{n} \tag{II}$$

worin R<sup>3</sup> ein Wasserstoffatom oder eine Alkylgruppe mit 1 bis 10 Kohlenstoffatomen ist, R<sup>4</sup> eine Alkylengruppe mit 1 bis 10 Kohlenstoffatomen ist, R<sup>5</sup> ein Wasserstoffatom oder eine Alkylgruppe mit 1 bis 10 Kohlenstoffatomen ist, n eine ganze Zahl von 1 bis 6 ist und m eine solche Zahl darstellt, daß der Durchschnittswert m x n bei 6 bis 80 liegt.

7. Zusammensetzung nach Anspruch 3, worin der Polyvinylether ein Polymer auf Vinyletherbasis ist, das die durch die allgemeine Formel (III) dargestellte Aufbaueinheit aufweist

worin R<sup>6</sup>, R<sup>7</sup> und R<sup>8</sup> jeweils ein Wasserstoffatom oder ein Kohlenwasserstoffradikal, insbesondere eine Alkylgruppe mit 1 bis 10 Kohlenstoffatomen sind; R<sup>9</sup> ein divalentes Kohlenwasserstoffradikal, insbesondere eine Alkylengruppe mit 1 bis 10 Kohlenstoffatomen oder ein Sauerstoffatom-enthaltendes Kohlenwasserstoffradikal mit 2 bis 20 Kohlenstoffatomen ist, das eine divalente Etherbindung aufweist; R<sup>10</sup> ein Kohlenwasserstoffradikal, insbesondere eine Alkylengruppe mit 1 bis 10 Kohlenstoffatomen ist; k einen Durchschnittswert von 0 bis 10 darstellt; R<sup>6</sup> und R<sup>10</sup> gleich oder verschieden voneinander in jeder Aufbaueinheit sein können; und R<sup>9</sup>, wenn eine Mehrzahl von Aufbaueinheiten vohanden ist, gleich oder verschieden sein kann.

8. Zusammensetzung nach Anspruch 4, worin der Polyvinylether ein Polymer auf Vinyletherbasis ist, das die durch die allgemeine Formel (III) dargestellte Aufbaueinheit aufweist

R<sup>6</sup> R<sup>8</sup> --(C-C-)-R<sup>7</sup> O(R<sup>9</sup>O)<sub>k</sub>R<sup>10</sup>

worin R<sup>6</sup>, R<sup>7</sup> und R<sup>8</sup> jeweils ein Wasserstoffatom oder ein Kohlenwasserstoffradikal, insbesondere eine Alkylgruppe mit 1 bis 10 Kohlenstoffatomen sind; R<sup>9</sup> ein divalentes Kohlenwasserstoffradikal, insbesondere eine Alkylengruppe mit 1 bis 10 Kohlenstoffatomen oder ein Sauerstoffatom-enthaltendes Kohlenwasserstoffradikal mit 2 bis 20 Kohlenstoffatomen ist, das eine divalente Etherbindung aufweist; R<sup>10</sup> ein Kohlenwasserstoffradikal, insbesondere eine Alkylengruppe mit 1 bis 10 Kohlenstoffatomen ist; k einen Durchschnittswert von 0 bis 10 darstellt; R<sup>6</sup> und R<sup>10</sup> gleich oder verschieden voneinander in jeder Aufbaueinheit sein können; und R<sup>9</sup>, wenn eine Mehrzahl von Aufbaueinheiten vohanden ist, gleich oder verschieden sein kann.

### Revendications

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- Composition d'huile pour machine réfrigérante qui comprend une huile de base et au moins un composé époxy.
  choisi dans l'ensemble consistant en oxyde de D-limonène, oxyde de L-limonène, oxyde d'α-pinène, et oxyde de
  L-carvone, ledit composé époxy étant mélangé avec ladite huile de base.
- 2. Composition selon la revendication 1, dans laquelle le ou les composés époxy choisis dans l'ensemble consistant en oxyde de D-Limonène, oxyde de L-limonène, oxyde d'α-pinène, et oxyde de L-carvone sont mélangés en une quantité comprise entre 0,05 et 10% en poids par rapport à la quantité totale de la composition.
  - 3. Composition selon la revendication 1, dans laquelle l'huile de base est au moins un composé contenant des atomes d'oxygène choisi dans l'ensemble consistant en polyglycol et poly(éther vinylique).
- 4. Composition selon la revendication 1, dans laquelle l'huile de base est un mélange d'un composé hydrocarboné et d'au moins un composé contenant des atomes d'oxygène choisi dans l'ensemble consistant en polyglycol et poly(éther vinylique).
- Composition selon la revendication 3, dans laquelle le polyglycol est un dérivé de polyoxyalkylèneglycol représenté
   par la formule générale (II)

$$R^{3}[(OR^{4})_{m}OR^{5}]_{n}$$
 (II)

dans laquelle R<sup>3</sup> représente un atome d'hydrogène ou un groupe alkyle contenant 1 à 10 atomes de carbone, R<sup>4</sup> représente un groupe alkylène contenant 1 à 10 atomes de carbone, R<sup>5</sup> représente un atome d'hydrogène ou un groupe alkyle contenant 1 à 10 atomes de carbone, n est un nombre entier de 1 à 6 et m est un nombre tel que la moyenne de m x n soit de 6 à 80.

Composition selon la revendication 4, dans laquelle le polyglycol est un dérivé de polyalkylèneglycol représenté
 par la formule générale (II)

$$R^{3}[(OR^{4})_{m}OR^{5}]_{n} \tag{II}$$

dans laquelle R<sup>3</sup> représente un atome d'hydrogène ou un groupe alkyle contenant 1 à 10 atomes de carbone, R<sup>4</sup> représente un groupe alkylène contenant 1 à 10 atomes de carbone, R<sup>5</sup> représente un atome d'hydrogène ou un groupe alkyle contenant 1 à 10 atomes de carbone, n est un nombre entier de 1 à 6 et m est un nombre tel que la moyenne de m x n soit de 6 à 80.

7. Composition selon la revendication 3, dans laquelle le pol(éther vinylique) est un polymère à base d'éther vinylique ayant le motif constitutionnel représenté par la formule générale (III):

$$R^{6}$$
  $R^{8}$   
| | |  
 $-(C - C) -$  (III)  
 $R^{7}$   $O(R^{9}O)_{k}R^{10}$ 

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dans laquelle R<sup>6</sup>, R<sup>7</sup> et R<sup>8</sup> représentent chacun un atome d'hydrogène ou un radical hydrocarboné, en particulier un groupe alkyle, contenant 1 à 10 atomes de carbone ; R<sup>9</sup> représente un radical hydrocarboné divalent, en particulier un groupe alkylène, contenant 1 à 10 atomes de carbone ou un radical hydrocarboné divalent contenant des atomes d'oxygène, à liaisons éther, contenant 2 à 20 atomes de carbone ; R<sup>10</sup> représente un radical hydrocarboné, en particulier un groupe alkylène, contenant 1 à 10 atomes de carbone ; k est un nombre compris entre 0 à 10 en moyenne ; R<sup>6</sup> à R<sup>10</sup> peuvent être identiques ou différents les uns des autres pour chaque motif constitutionnel ; et les R<sup>9</sup>, lorsqu'ils sont contenus plusieurs fois dans les motifs constitutionnels, peuvent être identiques ou différents.

8. Composition selon la revendication 4, dans laquelle le pol(éther vinylique) est un polymère à base d'éther vinylique ayant le motif constitutionnel représenté par la formule générale (III):

$$R^{6}$$
  $R^{8}$   
| | |  
-(C - C) - (III)  
| | |  
 $R^{7}$   $O(R^{9}O)_{k}R^{10}$ 

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dans laquelle R<sup>6</sup>, R<sup>7</sup> et R<sup>8</sup> représentent chacun un atome d'hydrogène ou un radical hydrocarboné, en particulier un groupe alkyle, contenant 1 à 10 atomes de carbone; R<sup>9</sup> représente un radical hydrocarboné divalent, en particulier un groupe alkylène, contenant 1 à 10 atomes de carbone ou un radical hydrocarboné divalent contenant des atomes d'oxygène, à liaisons éther, contenant 2 à 20 atomes de carbone; R<sup>10</sup> représente un radical hydrocarboné, en particulier un groupe alkylène, contenant 1 à 10 atomes de carbone; k est un nombre compris entre 0 à 10 en moyenne; R<sup>6</sup> à R<sup>10</sup> peuvent être identiques ou différents les uns des autres pour chaque motif constitutionnel; et les R<sup>9</sup>, lorsqu'ils sont contenus plusieurs fois dans les motifs constitutionnels, peuvent être

identiques ou différents.